5.2.3. GRAVIMETRIC STANDARDS

Calibration Scales

Numerous standards were prepared in 2000-2001. In total, 62 gravimetric standards were prepared and 89 working standards were filled at NWR during this period.

The calibration scales of N_2O, SF_6, CFC-12, CFC-11, CH_3CCl_3, CCl_4, and halon-1211 were examined with the aim of incorporating all HATS measurements, as well as CCGG N_2O and SF_6 flask measurements, on common scales. This involved analysis of numerous working standards used by the flask programs, airborne programs, and in situ programs. This work will continue into the near future and will include additional molecules.

A key element of this work involved the preparation of additional gravimetric standards for N_2O and SF_6 (Figures 5.22 and 5.23). Previous scales for these molecules had been defined by a limited number (four to six) of gravimetric standards. While these standards were useful for defining a scale over a wide concentration range, the lack of multiple standards with near-ambient concentrations presented difficulties in establishing the long-term stability of these scales. New primary standards were prepared from the same reagents used to establish the original scales. Secondary/tertiary standards were prepared from the new primary standards as well as from existing primary standards. The 2000 N_2O scale is about 1 ppb lower than the 1993 scale, and it is 0.5 ppb higher than that predicted using 300 and 330 ppb National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs). The 2000 SF_6 scale differs from the 1994 scale [*Geller et al.*, 1997] by less than 0.1 ppt, which is within the uncertainty associated with the 1994 scale.

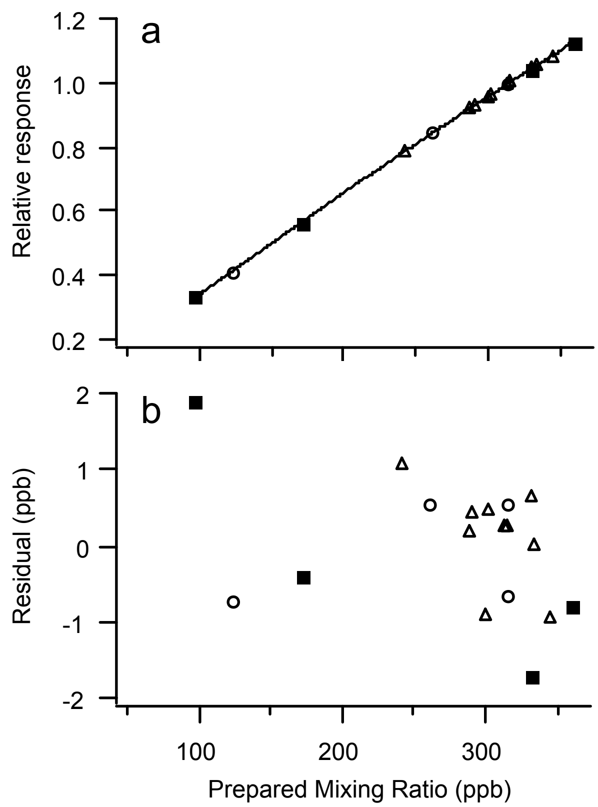

Fig. 5.22. (a) Second-order calibration curve and (b) residual, resulting from analysis of gravimetric standards that define the 2000 N_2O scale. Standards prepared from similar primary standards are shown as similar symbols.

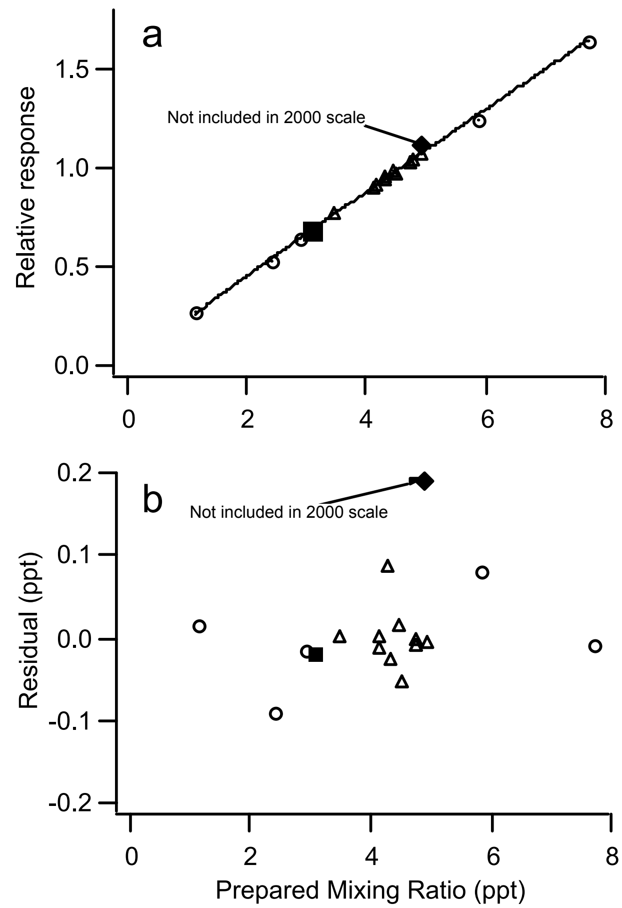

Fig. 5.23. (a) Second-order calibration curve and (b) residual, resulting from analysis of gravimetric standards that define the 2000 SF_6 scale. Standards prepared from similar primary standards are shown as similar symbols.

A scale based on a large number of standards makes it easier to identify outliers (standards that, for whatever reason, do not agree with the majority) (Figure 5.23). These new N_2O-SF_6 standards have also helped to improve the long-term stability of the N_2O and SF_6 scales (e.g., the loss or drift of a single standard does not affect the scale as much as it would if the scale were defined by only a few standards). More information on gravimetric standards used to define HATS scales, including a list of the standards used to define the new 2000 N_2O and 2000 SF_6 scales, is available on the CMDL/HATS website (http://www.cmdl.noaa.gov/hats/standard/scales.htm).

A second element of this work involved the analysis of reagent-grade materials used to prepare primary standards. The reagents used to prepare primary CH_3CCl_3, CCl_4, and CFC-12 standards were sent to NIST (Gaithersburg, Maryland) for purity analysis. No significant volatile impurities were found in CFC-12 or CCl_4 reagents. However, the CH_3CCl_3 reagent used to establish the 1996 CH_3CCl_3 scale [see *Hall et al*., 2001] was found to contain impurities amounting to approximately 6.4% (by mole). New high-purity reagent-grade CH_3CCl_3 was purchased from a different vendor (Sigma-Aldrich, St. Louis, Missouri.). The purity of this new reagent is approximately 99.8% based on the NIST analysis (99.9% according to the manufacturer's assay). New primary standards were prepared from this reagent. These new standards show a molar response that is roughly 5% higher than those prepared from the old reagent, which is consistent with the results of the reagent analysis. Development of a new CH_3CCl_3 scale is under way. It is expected that this new scale will be about 5% lower than the 1996 scale used in the publications of *Hurst et al*. [1997], *Volk et al*. [1997], *Butler et al*. [1999], *Montzka et al*. [1999, 2000], and *Romashkin et al*. [1999].

Gravimetric standards for carbonyl sulfide (COS) were prepared from newly purchased COS reagent. Several ppt-level standards were prepared in 29-L Aculife-treated aluminum cylinders. The stability of these standards is being evaluated. Two of five ppt-level standards are already showing signs of COS loss. Although many of the working standards used in the in situ program do not show COS loss, the viability of aluminum cylinders for COS at the ppt level is still being evaluated.

New gravimetric standards for CO were prepared in 1999-2000. These new standards helped to confirm that secondary standards prepared in 1989 had drifted and that a scale update was needed [*Tans et al*., 2001]. The scale will be maintained by preparation of new gravimetric standards every 2 years and by comparison of ppb-level standards to ppm-level NIST SRMs.

Calibration of Working Standards

Working standards continue to be calibrated using a four-channel gas chromatograph similar to those used for in situ measurements (CATS). The initial calibration of this instrument was established in 1999 by comparison of a working standard (natural air at ambient concentration) to gravimetric standards, as well as to previous working standards. Routine calibration is maintained by comparison of the working standard to five additional working standards (mixtures of natural and ultrapure air at concentrations ranging from 40% to 100% of ambient). These comparisons are performed every 1-2 months or after a significant change in GC operating parameters. Frequent analysis of these working standards enables detection of small changes in GC performance or response characteristics without depletion of gravimetric standards. Each set of gravimetric standards used to define a particular scale is analyzed yearly.

The routine analysis of the working standards also provides information on the day-to-day variability of the GC. This information can be used to provide an estimate of the uncertainties associated with the calibration of working standards using this instrument. Knowledge of the day-to-day variability is crucial if small changes (drift) are to be detected. Table 5.7 shows the precision over a single day and uncertainties over multiday periods, associated with the calibration of a working standard. The information in Table 5.7 is related only to the performance of the CATS instrument and does not describe the accuracy of the calibration scales. It is useful to assess how well two identical standards can be calibrated, or the degree to which two calibrations of the same standard, performed months or years apart, can be expected to agree (assuming that the standard is stable over this period). Instrument precision on a given day (Table 5.7) is often very good, 0.4 ppb for N_2O, for example. However, differences in the mean concentration determined on different days can occur because of the imprecise nature of the calibration method and small changes in response characteristics associated with changes in carrier gas purity, column condition, etc. For these reasons, standards are typically analyzed on 2-3 different days. Uncertainties associated with multiday calibrations are larger than the daily precision and decrease with additional analysis, as expected. Although it is impractical to analyze working standards over 10 days, these data provide an estimate of the best overall uncertainty achievable with the CATS calibration system.

New High-Pressure Cylinders

Aluminum cylinders are not ideal for the long-term storage of methyl halides. Air stored in Aculife-treated aluminum cylinders, particularly those purchased since 1998, tend to show decreases of CH_3Br and increases in CH_3Cl over time. The rate of change of these compounds is highly variable and cylinder specific. A small number of these cylinders seem to be relatively stable, but an alternative is clearly needed.

In an attempt to obtain gas cylinders that will be superior to aluminum cylinders for the long-term storage of methyl halides, several electropolished, stainless-steel cylinders were purchased. These cylinders are approved by the Department of Transportation for transport at pressures of 6200 kPa (900 psi). Preliminary stability testing involved filling cylinders with moist ultrapure air and moist natural air. No significant changes were observed in the ultrapure air samples (i.e., outgassing of compounds normally detected with CATS instruments was not observed).

TABLE 5.7. Precision and Uncertainties Associated with the Calibration of Working Standards

	Precision*	Uncertainty (3 days)†	Uncertainty (10 days)†
N_2O (ppb)	0.4	0.8	0.5
CFC-12 (ppt)	0.8	1.3	0.8
CFC-11 (ppt)	0.6	1.0	0.6
CFC-113 (ppt)	0.2	0.5	0.3
CH_3CCl_3 (ppt)	0.2	0.6	0.3
CCl_4 (ppt)	0.2	0.7	0.4
SF_6 (ppt)	0.03	0.04	0.02
Halon-1211 (ppt)	0.02	0.03	0.02

*Typical daily precision (expressed as $2\sigma/N^{0.5}$) associated with 8-10 comparisons of an unknown to a reference standard at ambient concentration. These data are similar to those of *Hall et al*. [2001].

†Uncertainties associated with a multiday calibration (95% confidence level). The uncertainties associated with the 3-day calibration are typical for the calibration of working standards used in the flask and in situ programs.